

# High frequency dielectric and magnetic anomaly at the phase transition in $\text{NaV}_2\text{O}_5$

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We found anomalies in the temperature dependence of dielectric and magnetic susceptibility of  $\text{NaV}_2\text{O}_5$  in the microwave and far infrared frequency ranges. The anomalies occur at the phase transition temperature  $T_c$ , at which the spin gap opens. The real parts of the dielectric constants  $\epsilon_a$  and  $\epsilon_c$  decrease below  $T_c$ . The decrease of  $\epsilon_a$  (except for the narrow region close to  $T_c$ ) is proportional to the intensity of the x-ray reflection appearing at  $T_c$ . The dielectric constant anomaly can be explained by the zigzag charge ordering in the  $ab$ -plane appearing below  $T_c$ . The anomaly of the microwave magnetic losses is probably related to the coupling between the spin and charge degrees of freedom in vanadium ladders.

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## I. INTRODUCTION

Two inorganic compounds,  $\text{CuGeO}_3$  and  $\text{NaV}_2\text{O}_5$ , were extensively studied as quasi-one-dimensional (1D) magnets containing the chains of spins  $S = \frac{1}{2}$  coupled by the antiferromagnetic Heisenberg exchange. Both materials show 1D behavior of the susceptibility at high temperatures and the phase transition into the spin-gap state at low temperatures. The lattice deformation appears simultaneously with the spin-gap opening at the transition temperature  $T_c$ . The lattice deformation includes the doubling of the lattice period in the spin-chain direction and the spin gap is believed to be a result of the corresponding alternation of the exchange constants along the chains.

The phase transition in  $\text{CuGeO}_3$  is generally considered to be a spin-Peierls transition. The driving force of this transition is the collective spin-lattice instability with the gain in the energy of the spin chains exceeding the loss in the lattice energy.<sup>1,2</sup> The experimental data on  $\text{CuGeO}_3$  are in a good agreement with the theoretical results for the antiferromagnetic spin- $\frac{1}{2}$  chains coupled to the lattice.<sup>3</sup> Some deviations from the ideal spin-Peierls behavior found for  $\text{CuGeO}_3$  are also well-understood. They are related to a considerable interchain interaction (the interchain exchange being about 0.1 of the intrachain exchange<sup>3</sup>) and a strong next-nearest-neighbor exchange (about 0.3 of the nearest-neighbor exchange<sup>4</sup>).

For some time  $\text{NaV}_2\text{O}_5$  was considered as the second inorganic spin-Peierls system. The 1D-magnetic structure of  $\text{NaV}_2\text{O}_5$  was first associated with the chains of  $\text{V}^{4+}$ -ions (spin  $S=1/2$ ) along the  $b$ -axis of the orthorhombic crystal separated by the chains of nonmagnetic  $\text{V}^{5+}$  ions.<sup>5,6</sup> This structure with inequivalent vanadium sites was recently questioned in Refs. 7–10. On the basis of the new structure refinement studies of the high-temperature phase of  $\text{NaV}_2\text{O}_5$  the new ladder-type structure with equivalent V-sites was suggested.<sup>7,8</sup> The ladders are oriented along the  $b$ -axes with the rungs along the  $a$ -axis. There is one electron per rung and the spin- $\frac{1}{2}$  chains are formed by the electrons localized on V-O-V molecular orbitals on rungs and coupled by the exchange interaction along the  $b$ -direction. In this structure the charge of V-ions fluctuates, its average value being 4.5.

Recent experimental data,<sup>11</sup> as well as the theoretical arguments,<sup>12–14</sup> suggest that the phase transition in  $\text{NaV}_2\text{O}_5$  can be a result of some charge ordering rather than the spin-Peierls instability. Two kinds of such an ordering were considered. In the model of Ref. 12 the electrons below  $T_c$  become localized on one leg of each ladder, as in the initially proposed high temperature structure<sup>5</sup>. In this model one has to invoke an extra mechanism to account for the spin gap at low temperatures. In the second model<sup>13,14</sup> the electrons (or the  $\text{V}^{4+}$ -ions) form zigzags on each ladder. The opening of the spin gap in this scenario is a direct consequence of the charge ordering. The

optical spectra of  $\text{NaV}_2\text{O}_5$ <sup>15,16</sup> were first interpreted as an indication on the presence of inequivalent V-sites even at room temperature. However, these spectra could also be explained by the presence of only a short range charge order with relatively slow charge fluctuations. An extra confirmation that the phase transition in  $\text{NaV}_2\text{O}_5$  is not an ordinary spin-Peierls transition comes from the study of thermal conductivity: in contrast to the spin-Peierls system  $\text{CuGeO}_3$ , the thermal conductivity of  $\text{NaV}_2\text{O}_5$  has a huge anomaly below  $T_c$ , which can be naturally explained by the charge ordering.<sup>17</sup>

Further information about the charge subsystem close to the phase transition point can be gained by studying the dielectric constant. Measurements of the dielectric constant at the frequency of 1 KHz along three principal directions were performed in Ref. 18. An anomaly with a strong anisotropy with respect to the electric field orientation signifying the rearrangement of the charge in  $\text{NaV}_2\text{O}_5$  has been found.

In this paper we present combined measurements of the real and imaginary part of the dielectric and magnetic susceptibility of  $\text{NaV}_2\text{O}_5$  at the microwave frequency of 36 GHz and of the refractive index in the far infrared range. For comparison the measurements of the same parameters were performed also for  $\text{CuGeO}_3$ . Our results on  $\text{NaV}_2\text{O}_5$  confirm the presence of strong anomalies in the dielectric constant along the *a*- and *c*-directions, although the type of the anomaly for the *c*-direction is different from the one found in Ref. 18. The anomaly in  $\epsilon_a$  is naturally explained by the picture of the zigzag charge ordering suggested in Ref. 13,14. Possible reasons for the anomaly in  $\epsilon_c$  are discussed and further experiments to check this picture are suggested.

## II. EXPERIMENT

We studied the complex microwave dielectric and magnetic susceptibilities by measuring the temperature dependence of the resonance frequency and of the *Q*-factor of the microwave  $\text{TE}_{104}$  cavity of the size  $20 \times 7.2 \times 3.4$  mm. The resonance frequency *f* of the empty cavity is 36 GHz. The presence of a sample shifts the resonance frequency of the cavity. When the sample in the form of a thin plate is placed at the maximum of the microwave electric field  $\mathbf{E}_{mw}$ , with the plane of the plate parallel to the electric field, the resonance frequency of the cavity should be shifted by the value  $\delta f$ :

$$\frac{\delta f}{f} = -2 \frac{(\epsilon' - 1)v}{V}. \quad (1)$$

Here *v*, *V* are the volumes of the sample and of the cavity respectively,  $\epsilon'$  is the real part of the dielectric constant.

When the sample plane is oriented perpendicularly to the field  $\mathbf{E}_{mw}$ , the shift of the frequency is given by the relation:

$$\frac{\delta f}{f} = -2 \frac{(\epsilon' - 1)v}{\epsilon' V}. \quad (2)$$

In this case the frequency shift is smaller due to the depolarization factor effect. Formulae (1) and (2) are valid in the quasistatic approximation when the sample is small in comparison with the length of the electromagnetic wave.

The imaginary part of the dielectric susceptibility  $\epsilon''$  affects the *Q*-factor and results in a diminishing of the microwave power *U* transmitted through the cavity. The relative change of *U* is given by the relation:

$$\frac{\delta U}{U} = -4Q\epsilon'' \frac{v}{V}. \quad (3)$$

The analogous relations could be used to determine the magnetic permeability,  $\mu = \mu' + i\mu''$ , in the case when the sample is placed at a maximum of the microwave magnetic field.

The sample used for the microwave susceptibility measurements had the dimensions  $1 \times 1 \times 0.3$  mm and, thus, was much smaller than the half of the length of the standing electromagnetic wave in the cavity (5 mm). This fact enables us to separate the magnetic and dielectric susceptibilities by positioning the sample at different points of the cavity. The *a*- and *b*-directions were lying in the plane of the plate, the *c*-axis being perpendicular to the plate.

The change of the refractive index *n* with temperature was measured in the frequency range between 1.2 and 3.0 THz by registering the interference pattern at different temperatures in the transmittance spectra of thin (14-110 μm) plates of  $\text{NaV}_2\text{O}_5$  single crystals cleaved perpendicular to the *c*-direction. The spectra were measured using the BOMEM DA3.002 Fourier transform spectrometer at the resolution of 0.2-2.0  $\text{cm}^{-1}$ . The incident light was polarized either along the *a*-axis ( $\mathbf{E} \parallel a$ ) or along the *b*-axis ( $\mathbf{E} \parallel b$ ). We have also performed  $\mathbf{E} \parallel c$  measurements at room temperature.

The position  $\nu_m$  (in wavenumbers) of the *m*-th maximum in the transmittance spectrum is given by the expression

$$\nu_m = \frac{m}{2dn}, \quad (4)$$

where *d* is the thickness of the plate. We determined the three principal values of the refractive index along the *a*-, *b*-, and *c*-axes by measuring the distance between the adjacent maxima of the interference pattern.

The relative changes of the dielectric constant  $\epsilon'$  were found from the measured shifts of the interference maxima according to the relation

$$\frac{\delta \epsilon'}{\epsilon'} = 2 \frac{\delta n}{n} = -2 \frac{\delta \nu_m}{\nu_m}. \quad (5)$$

The dielectric constant is the total polarizability of the sample divided by the sample volume. The change of

the sample size at the phase transition was observed by studying the thermal expansion.<sup>19</sup> The relative change of the sample size in the vicinity of the phase transition was of the order of  $10^{-4}$ . In our microwave measurements the change of the resonator frequency is caused by the total polarizability of the sample. Therefore the frequency of the resonator is not affected by the change of the sample size if it takes place without the change of the total polarizability. Because we calculate the value of  $\delta\epsilon'$  supposing the constant size of the sample, the experimental data on the microwave susceptibility can not be attributed to the thermal expansion.

On the contrary, the change of the refractive index measured at far infrared frequency by the observation of the interference pattern should be influenced by a change of the sample thickness and volume. In the case of the constant total polarizability the resulting relative change of the refractive index is to be of the order of the relative change of the size.

Single crystals of stoichiometric  $\text{NaV}_2\text{O}_5$  used in our experiments have been obtained by a melt growth method using  $\text{NaVO}_3$  as a flux. The details of the growth procedure are described in Ref. 20. Our samples were of the same growth procedure as used in Ref. 21. The temperature  $T_c$  of the phase transition obtained from the beginning of the magnetic susceptibility drop is  $36 \pm 0.5\text{K}$ .

### III. EXPERIMENTAL RESULTS

#### A. Microwave measurements

The shift of the resonant frequency of the cavity produced by the sample at  $T=40\text{K}$  was of about 400 MHz both for  $\mathbf{E}_{mw} \parallel b$  and  $\mathbf{E}_{mw} \parallel a$ . It corresponds to the dielectric constant values  $\epsilon'_{a,b} = 12 \pm 1$ .

For  $\mathbf{E}_{mw} \parallel c$ , when the microwave electric field is perpendicular to the plate, the shift of the resonator frequency was only  $40 \pm 15$  MHz. Either the small value of  $\epsilon'_c$  or the depolarization effect could result in this frequency shift which is much smaller than in the case of  $\mathbf{E}_{mw} \parallel a$  or  $\mathbf{E}_{mw} \parallel b$ . Thus, the absolute value of  $\epsilon'_c$  could not be estimated accurately enough: following the formula (2) we obtain the value  $\epsilon'_c$  between 4 and infinity. However, the frequency shift of the resonator and the value of relative change of  $\epsilon_c$  at the phase transition can be measured quite accurately. We used the value  $\epsilon'_c = 8$  obtained in quasistatic measurements<sup>18</sup> and in the far infrared experiments described below, for the calculations of  $\delta\epsilon_c$  according to the formula (2).

The temperature dependence of the change of the dielectric function was derived from the dependence of the resonator frequency shift with respect to the frequency at  $T=1.5\text{K}$ . The value of the change of the imaginary part was derived from the temperature dependence of the transmitted signal relative to the reference value of this signal at 40 K.

The temperature dependence of the change of the dielectric susceptibility is shown in Fig. 1. The real part of the dielectric constants  $\epsilon'_{a,c}$  decreases below the phase transition temperature, while the real part of  $\epsilon_b$  does not show any observable change. The imaginary part of  $\epsilon_b$  exhibits a well-pronounced peak. The change of the imaginary part of  $\epsilon_a$  and  $\epsilon_c$  were found to be smaller than the apparatus noise level.

A change in the response of the sample to the microwave magnetic field was only found for the imaginary part of the magnetic susceptibility. These results are shown in Fig. 2.

We reexamined the  $\text{CuGeO}_3$  crystals studied in Refs. 22,23 and have not found any changes of the dielectric and magnetic susceptibilities of comparable values.

#### B. Far infrared measurements

For the frequency of 1.2 THz we have obtained the following values of  $\epsilon'$  at room temperature:  $\epsilon'_a = 15.0 \pm 0.6$ ,  $\epsilon'_b = 10.2 \pm 0.2$ ,  $\epsilon'_c = 7.5 \pm 0.2$ . These data are close to those for  $\epsilon'$  at zero frequency found earlier from the fitting of the reflectivity spectra of  $\text{NaV}_2\text{O}_5$  single crystals by the model of independent oscillators.<sup>24</sup>

Fig. 3 shows the temperature dependence of the relative change of the refractive index at different far infrared frequencies for the electric field polarized along the  $a$ - and  $b$ -axes. Simultaneously with diminishing of the refractive index  $n_a$ , the absorption present in the low-frequency region of the far infrared spectrum of  $\text{NaV}_2\text{O}_5$  above  $T_c$  decreases markedly when temperature decreases below  $T_c$  (see the inset of Fig. 3 and Ref. 16). We checked that despite these changes of the absorption coefficient, equation (5) allows us to determine the changes of  $n_a$  with sufficiently good precision. The relative change of the refractive index is of about 0.05 and corresponds to the change of the dielectric constant that is approximately twice as large as the value found at the microwave frequency of 36 GHz.

We have not found any observable changes of  $\epsilon'_b$  (or  $n_b$ ). Unfortunately, we could not observe the interference pattern for  $\mathbf{E} \parallel c$  polarization at low temperatures and, hence, to detect the possible changes of  $\epsilon'_c$ .

### IV. DISCUSSION

The observed dielectric anomalies could, in principle, arise from (i) an anomalous thermal expansion of  $\text{NaV}_2\text{O}_5$  at  $T_c$ ,<sup>19</sup> (ii) a change of the lattice polarizability and (iii) a rearrangement of electrons below  $T_c$ .

As it was described in Sec.II the microwave measurements of  $\epsilon$  are insensitive to changes of a sample size, thus the reason (i) could not result in the dielectric constant data shown in Fig. 1. Besides that, the thermal expansion anomaly<sup>19</sup> could result in changes of  $\epsilon'$  of the order

of  $10^{-4}$  which is 2 orders of magnitude smaller than the observed value both at microwave and far infrared frequencies.

As for (ii), the changes in the lattice polarizability should be accompanied by the corresponding changes in the phonon spectrum below  $T_c$ .<sup>16</sup> Our estimates show that the new modes that appear below  $T_c$  cannot account for the observed change of  $\epsilon'$  due to their relatively small oscillator strengths.

The observed dielectric anomalies of relatively large amplitudes agree with the conclusion about the charge ordering at  $T_c=35\text{K}$  in  $\text{NaV}_2\text{O}_5$ . Analyzing the form of the temperature dependence of  $\epsilon$  one can choose an adequate model of the charge ordering. The model with a localization of electrons on one leg of the ladder<sup>12</sup> corresponds to the ferroelectric ordering with the spontaneous electric polarization along the  $a$ -axis. In this case the peak in the temperature dependence of  $\epsilon'_a$  should be observed. Since the anomalies found in the real part of the dielectric constant have the form of steps (typical for the antiferroelectric transition) rather than peaks, we conclude that the charge ordering occurs without a generation of a macroscopic dipole moment. The charge ordering of an antiferroelectric type may be in the form of the zigzag distribution of  $\text{V}^{4+}$ -ions as described in Refs. 13,14. In this case the decrease of the dielectric constant  $\epsilon'_a$  can be attributed to the shrinking of the electron clouds along the  $a$ -direction due to the localization of electrons on the distinct V-sites, instead of being smeared along the V-O-V orbitals. The observed diminishing of the optical absorption coefficient in the frequency range studied (1.2-3.0 THz) below  $T_c$  is probably also connected with the above mentioned shrinking of the electron clouds, the absorption itself being of an electronic origin (see, in particular, Ref. 24).

The coupled spin and charge degrees of freedom in vanadium ladders were described in Ref. 13 using the spin-isospin Hamiltonian. The isospin concept is introduced for the description of a charge ordering: Isospin  $\tau_i^z = +1/2$  corresponds to the electron localized on one end of the rung  $i$ , while  $\tau_i^z = -1/2$  describes the electron localized on the other end. A charge ordering would result in the formation of the dipole moments  $d_i^z$  along  $a$ -direction on the rungs, with  $d_i^z \propto \tau_i^z$ . The zigzag ordering corresponds here to  $\tau^z$ -antiferromagnetism. The coupling of an external electric field along the  $a$ -axis to the local (rung) order parameter is given by the term  $-E_z \tau_i^z$ , similar to the coupling  $-H_z s_i^z$  in magnetic systems, and the resulting behavior of  $\epsilon'_a$  should be similar to the behavior of the parallel magnetic susceptibility,  $\chi_{\parallel}$ , in an antiferromagnet. This consideration is in a qualitative agreement with the experimental data shown in Fig. 1.

Using the Landau mean field approach near  $T_c$ , one can show that the decrease of the dielectric susceptibility is proportional to the square of the charge order parameter, i.e., the value of  $\delta\epsilon'_a$  is proportional to the intensity of the additional x-ray reflexes that appear at  $T_c$ . As

shown in the inset of Fig. 1, there is, indeed, a good correlation below  $\sim (T_c - 2\text{K})$  between  $\delta\epsilon'_a$  and the x-ray intensity measured in Ref. 25. There is some deviation of the data close to and above  $T_c$  - the value of  $\delta\epsilon'_a$  does not vanish at  $T_c$  and shows a tail up to  $T - T_c \approx 8\text{K}$ . This deviation above  $T_c$  can naturally be ascribed to the existence of short-range charge ordered areas which are fluctuating in some frequency range. These fluctuations give rise to the dynamic dielectric susceptibility above  $T_c$ , but are averaged out and vanish when the susceptibility is measured on a large time scale as it was observed at 1KHz in Ref. 18.

The nature of the behavior of the dielectric constant  $\epsilon'_c$  is less clear, especially, in view of the difference in the anomaly of  $\epsilon'_c$  obtained in our measurements (see Fig. 1) and in the quasistatic measurements of Ref. 18, where the  $\lambda$ -type anomaly was observed for  $\epsilon'_c$  instead of the step-like behavior shown in Fig. 1.

Both these measurements manifest the appearance of local dipole moments along the  $c$ -direction at the transition temperature. Possible origin of such moments may be, e.g., the shifts of the V-ions within  $\text{O}_5$ -pyramids along  $c$ -direction. The charge ordering (localization of the electrons on particular V ions) accompanied by the shifts of these ions along the  $c$ -direction can modify the local dipole moments in  $c$ -direction.

From the crystal structure of  $\text{NaV}_2\text{O}_5$  one would then again expect an antiferroelectric ordering of such dipoles, which would give the behavior of  $\epsilon'_c$  consistent with the one observed in the present work (see Fig. 1). The reason for different type of the  $\epsilon'_c$  anomaly observed in our measurements and in quasistatic measurements of Ref. 18 is not clear at present. A possible explanation might be related to the small but measurable conductivity of  $\text{NaV}_2\text{O}_5$  single crystals which has a peak of nearly 50 percents in amplitude at  $T_c$ .<sup>26</sup> The conductivity contributes only to the imaginary part of the microwave dielectric constant and at 40 K the contribution is of the order of  $10^{-7}$ . Thus, the conductivity is too small to affect the results of the microwave measurements. However, the influence of this small conductivity on the results of the electric capacity measurements at 1KHz<sup>18</sup> could be significant, because the observed value of conductivity results in the capacitor discharge time of about  $10^{-3}$  sec. Therefore, the electric field potential within the capacitor might be disturbed by a leakage current and this fact might result in an additional change of the capacity. Further experiments are needed to elucidate this point and also to check whether the anomalies in  $\epsilon'_c$  are indeed related to the shifts of V ions along the  $c$ -axis below  $T_c$  as argued above.

The picture of the phase transition in  $\text{NaV}_2\text{O}_5$  as being mainly of the charge-ordering type with some degree of a short-range order persisting above  $T_c$  is also qualitatively consistent with the behavior of the dielectric losses  $\epsilon''$  shown in Fig. 1. There should definitely exist slow enough charge fluctuations close to  $T_c$ , which would give rise to the absorption of the microwave power. Why is

the anomaly in  $\epsilon''$  the most pronounced for the electric field directed along  $b$ -axis is not clear yet.

Correspondingly, a coupling of the charge (and lattice) degrees of freedom to spins, definitely present in this compound, should result in magnetic losses, which were indeed observed (see Fig. 2). This coupling originates from the Pauli principle, which relates the symmetry of the spatial and spin parts of the wavefunction of two exchange-coupled electrons from the neighboring rungs of the ladder.<sup>13</sup> As a result, triplet excitations on the ladder rungs could carry a dipole moment.<sup>15</sup>

Note that the peak in the imaginary part of the magnetic susceptibility is of significant value and exceeds several times the value of the real part of the susceptibility at  $T_c$ . Therefore, the fluctuations of the spin gap alone could not explain the peak of magnetic losses and such peak is indeed not observed in  $\text{CuGeO}_3$ , where the charge ordering is absent.

## V. CONCLUSIONS

The anomalies of the dielectric and magnetic susceptibility in the microwave and far infrared frequency range were found. These anomalies are in agreement with the zigzag model of the charge ordering at the phase transition in  $\text{NaV}_2\text{O}_5$ . The observation of the pronounced dielectric constant anomaly and of the peak in magnetic losses at  $T_c$  indicates that the nature of the spin gap opening in  $\text{NaV}_2\text{O}_5$  is different from that of  $\text{CuGeO}_3$ .

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## Figure captions

Fig.1 Temperature dependence of the real and imaginary parts of the dielectric constant at the frequency 36 GHz. The inset demonstrates the comparison of the measurements of  $\delta\epsilon'_a$  (present work) and of the intensity  $I$  of the x-ray reflexes<sup>25</sup>:  $\alpha = 1 - \delta\epsilon'_a(T)/\delta\epsilon'_a(45K)$ .

Fig.2 Temperature dependence of the change of the imaginary part of the magnetic permeability at the frequency 36 GHz.

Fig.3 Temperature dependence of the relative change of the refractive index  $n_a$  at the frequency 1.1 THz ( $\square$ ), 1.4 THz ( $\triangle$ ), 1.9 THz ( $\nabla$ ), 2.2 THz ( $\diamond$ ), 2.6 THz ( $\circ$ ),

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2.8 THz ( $\times$ ), 3.1 THz (+) and  $n_b$  at 3.1 THz ( $\bullet$ ). Inset presents the temperature dependence of the integrated intensity of the far infrared absorption  $I = \int_{1.0 \text{ THz}}^{12 \text{ THz}} \beta(\nu) d\nu$ ,  $\beta$  being the absorption coefficient.

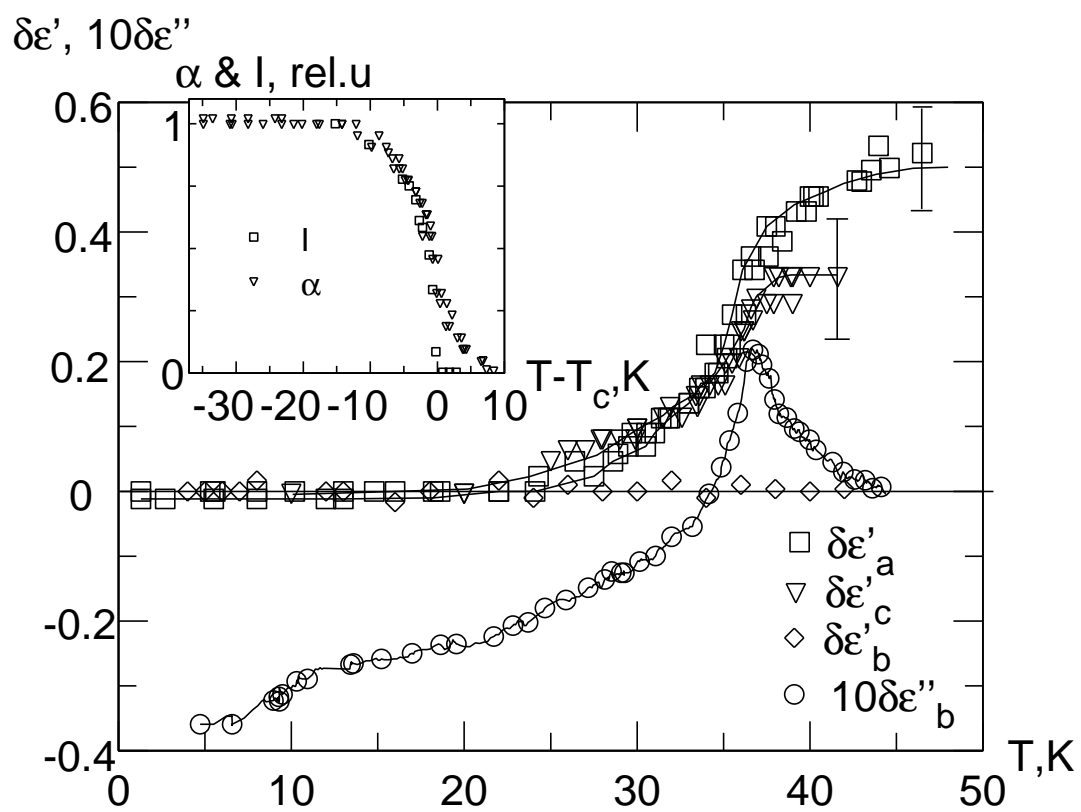


Fig.1 Smirnov et.al

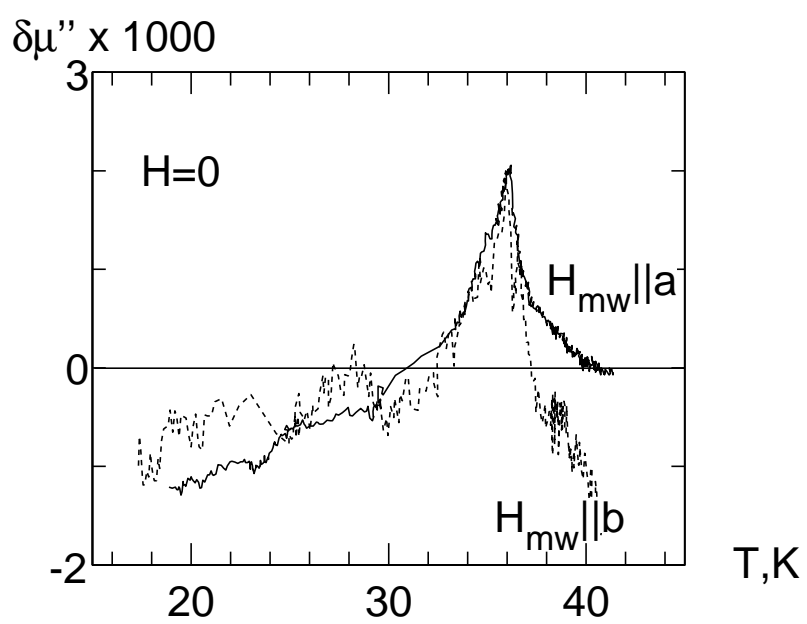


Fig.2 Smirnov et al



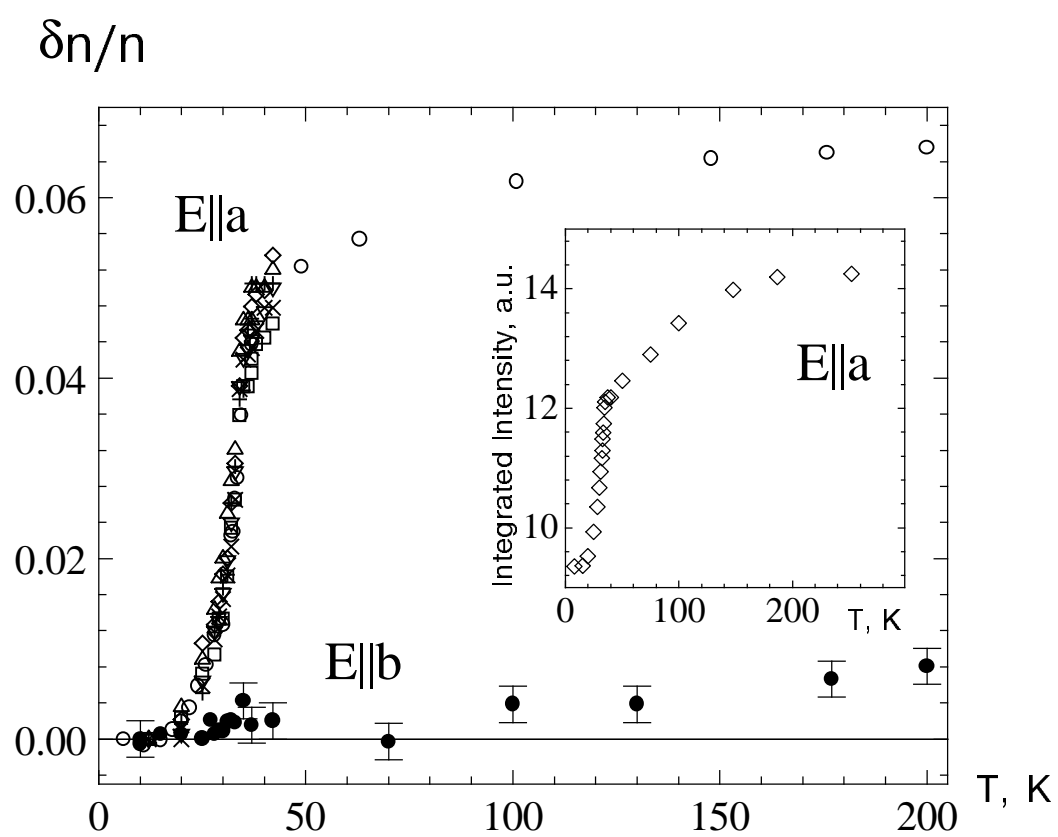


Fig. 3 Smirnov et. al.